

# **Pilot Demonstration of Hexavalent Chrome Removal and Recovery from ALC Waste Waters for Toxic Sludge Volume Reduction**

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## **ABSTRACT**

This paper reports on the successful pilot field tests for assessing the effectiveness of using Anion Liquid Ion Exchange (A-LIX) technology for removal and recovery of toxic but useful hexavalent chromium from U.S. Air Force Air Logistics Centers' (ALC's) industrial wastewater streams. The A-LIX field-testing demonstrated high system operability and excellent  $\text{Cr}^{\text{VI}}$  removal and product concentration. For feed streams with average  $\text{Cr}^{\text{VI}}$  concentrations of 6000 ppb, the field unit consistently produced a raffinate having less than 50 ppb  $\text{Cr}^{\text{VI}}$ . At the same time, the system was able to produce a  $\text{Cr}^{\text{VI}}$  concentrate of greater than 20,000 ppm.

Implementation of the A-LIX system has the potential to reduce sludge waste production at Warner Robins ALC alone by 276 tons per year. Rather than producing sludge as the current precipitation process does, the A-LIX system would produce a potentially reusable  $\text{Cr}^{\text{VI}}$  concentrate. It is concluded that the A-LIX process represents an excellent technical and good economic solution reducing USAF chromium plating shop waste. Therefore it is recommended to proceed to the next step, construction of a prototype commercial unit.

## **INTRODUCTION**

The U.S. Air Force seeks solutions to reduce or eliminate the large volumes of toxic waste sludges that are currently produced at its industrial wastewater treatment plants (IWTs) servicing its ALC's. These sludges contain varying quantities of hazardous materials, such as heavy metals, waste oils, and halogenated waste. Increasingly stringent environmental discharge regulations and rising disposal costs make it cost efficient to identify, evaluate, and develop candidate technologies to minimize the volume and/or toxicity of these sludges. The work reported in this paper supports this USAF goal through the development of technology for the recovery of hexavalent chromium, a high performance but toxic material, from ALC spent process liquors to reduce the amount of hazardous waste landfilled.

**Objective.** The objective of this work was to evaluate, at a pilot scale, the application of A-LIX technology for the removal of toxic hexavalent chromium from industrial process wastewater streams. The specific objectives for the project were (1) to validate continuous A-LIX processing for removal and recovery of toxic hexavalent chromium at ALC IWTPs, and (2) to collect process data and use it to prepare an engineering assessment for the scale-up of A-LIX to a commercial full-scale unit.

**Background.** Screening testing during Phase I of the program identified A-LIX as the preferred hexavalent chrome recovery technology for piloting in Phase II. A-LIX promised to allow not only the removal of trace hexavalent chromium, but also its recovery and concentration to a useful product in one continuous, low maintenance operation. In the A-LIX process, anionic  $\text{Cr}^{\text{VI}}$ , i.e.  $\text{HCrO}_4^-$ ,  $\text{CrO}_4^{2-}$ , and  $\text{Cr}_2\text{O}_7^{2-}$  ions, are recovered by reversible ion pairing with a protonated (cationic) water imiscible tertiary amine, Alamine<sup>®</sup> 336 (Henkel America, Inc.). The field trials took place at Warner Robins Air Logistic Center (WR-ALC) during the spring and summer of 1997. The WR-ALC IWTP #2 receives about 40,000 gallons per day of spent process wastewater containing 1000 to 10,000 ppb  $\text{Cr}^{\text{VI}}$  along with other impurities from the plating, conversion coating, and painting operations. These  $\text{Cr}^{\text{VI}}$  levels are substantially above regulated discharge levels (100 ppb). Field-testing occurred at Warner Robins ALC using a slipstream of effluent from the chromium-plating sump to IWTP #2. During this testing, data were collected on the effectiveness of E/A ratio, throughput rates, impeller tip speeds, and best means for pH control.

## PILOT PLANT DESCRIPTION AND OPERATION

The 1.5 liters per minute pilot-plant was cart mounted for portability. The separations component of the pilot-plant is a Robatel SX-4.0 four-stage mixer-settler unit (Figure 1). Added support equipment for the mixer-settlers included tanks, pumps, and filters. Instrumentation included pH meters, flowmeters, pressure gages, and temperature indicators.  $\text{Cr}^{\text{VI}}$  extraction was controlled using pH swing. The pH was automatically controlled between 3.5 and 6 for the extraction step using 10 percent sulfuric acid. Control of pH in the stripper was through occasional addition of caustic to internally recycled sodium carbonate solution.

During the four months of testing, the pilot unit ran very steadily, needing little attention to maintain a particular operating configuration. Liquids flowed under gravity from stage to stage without plugging. Interfaces between the aqueous and extractant phases remained steady in the settlers. No flooding in any of the tanks or mixer-settlers occurred. The stirrer-pumps performed well, varying no more than 1 rpm from their ~1000 rpm set points per day. An entrainment coalescing oil/water separator was included with the unit to minimize losses of extractant to the raffinate.

Samples were collected and analyzed after the system had time to approach steady state conditions. The following flow streams were sampled: Extractant phase, Extraction raffinate, Final raffinate (post-O/W separator), Stripping solution, and Feed solution. In addition, mixer emulsions were sampled and E/A ratios measured.  $\text{Cr}^{\text{VI}}$  analyses were performed in real time using the Hach Company selective Diphenylcarbazide Colorimetric method. This method was found to be ideal for field-testing.

## RESULTS AND DISCUSSION

A sample of the operating conditions for feed pH  $\sim 3.5$  are shown with corresponding  $\text{Cr}^{\text{VI}}$  raffinate concentrations in Table 1. The A-LIX system attained the 50-ppb target  $\text{Cr}^{\text{VI}}$  concentration during the majority of the test runs. The results presented in Table 1 include a test of the value for acidification of the feed stream with 10 percent sulfuric acid to a pH of approximately 3.5 to optimize  $\text{Cr}^{\text{VI}}$  recoveries. The average standard deviation was 10 ppb for runs that met the 50 ppb  $\text{Cr}^{\text{VI}}$  target raffinate concentration (all but one, which was at the highest feed flow rate). Due to the range in values of flowrates, feed concentrations, and pH's tested (not shown), it is concluded that acidification does not appear necessary for high  $\text{Cr}^{\text{VI}}$  recovery yields.

The two stripping units functioned without any mechanical or hydraulic problems. Occasional manual additions of 10 percent NaOH were used to maintain a pH of at least 11 in each unit. In a similar manner, but less frequently, additions of 10 percent  $\text{Na}_2\text{CO}_3$  were added when the buffering capacity of the strip solution diminished (pH drop too rapid).

Two percent Alamine<sup>®</sup> 336 extractant solution was tested but it was not possible to operate at extractant/feed (E/A) ratios of 1/5 or lower. Therefore, the remaining tests were run with a 5 percent Alamine 336<sup>®</sup> extractant solution which was found to perform well.

As expected, E/A ratio affected  $\text{Cr}^{\text{VI}}$  recoveries. There was only one run that did not have an average effluent concentration below 50-ppb (Table 1). This high residual is interpreted to be due to insufficient phase mixing at the high feed throughput and an above average feed concentration, 775 ml/min and 10,500 ppb  $\text{Cr}^{\text{VI}}$  respectively. Values as high as 646 ml/min feed throughput, and 1/9 E/A ratio were obtained in runs that produced acceptable effluent concentrations. These parameter values indicate that a basis of 600 ml/min feed throughput (3 min residence time) and 1/6 E/A ratio are conservative recommendations for a full scale A-LIX system.

Measurement of throughput rates provided the retention time,  $\tau$ , for mixing and settling. Each mixer was operated with  $\tau$  equal to about 3 minutes, and each settler with  $\tau$  equal to about 15 minutes. Higher throughput rates produced lower retention times, but resulted in emulsion carry over to the raffinate. Therefore, improved engineering design enhancements in phase coalescence would be required if higher throughput rates are desired. Previous test data indicate that chemical equilibria are not limiting at these conditions.

By varying the mixing impeller tip speeds in the extraction units, it was found that 1152 rpm produced too fine of an emulsion that led to a hazy raffinate. A small reduction in the impeller tip speed to 1125 rpm produced a clear raffinate. Therefore tests were performed at this lower rate.

Figure 2 shows how the concentration of  $\text{Cr}^{\text{VI}}$  in the first stripping unit continually increased during A-LIX operation. To evaluate whether the system could produce a highly concentrated  $\text{Cr}^{\text{VI}}$  solution, the strip solution in the first stripping unit was spiked with  $\text{Cr}^{\text{VI}}$ . The strip solution was first spiked to  $\sim 10,000$ -ppm  $\text{Cr}^{\text{VI}}$  and then to  $\sim 20,000$ -ppm  $\text{Cr}^{\text{VI}}$ . As Figure 3 shows, the system produced a consistent raffinate of low  $\text{Cr}^{\text{VI}}$  concentration despite these high product  $\text{Cr}^{\text{VI}}$  concentrations. Figure 3 also clearly illustrates the need for two extraction stages. With a feed concentration of about 6400 ppb  $\text{Cr}^{\text{VI}}$ , the concentration after one stage was about 180ppb and the concentration after the second stage was about 15 ppb.

In order to assess the reuse or market value of the concentrated  $\text{Cr}^{\text{VI}}$  product solution an unspiked sample of the concentrate was analyzed (Table 2). These results show the hexavalent

chrome to be quite pure with the exception of the added sulfate (Table 2). This sulfate is not expected to hinder recycle of the hexavalent chrome. The sulfate accumulation rate in the strip solution would be greatly reduced if the pH in the extraction units were maintained at 4.5 rather than 3.5. Hence higher (unadjusted) pH is recommended for commercial operation.

### A-LIX ECONOMIC ANALYSIS

An economic analysis of a conceptual, full scale A-LIX system for installation at the WR-ALC IWTP #2 was performed. The following values are the basis for the analysis: feed of 80,000 gallons/day (GPD) and 6 ppm  $\text{Cr}^{\text{VI}}$ , extraction E/A ratio of 1/6, extraction pH of 4.5 and stripping pH of 11, mixer residence times of 3 minutes, settler residence times of 16 minutes, 56 ppm extractant phase in raffinate.

The cost of each of the four mixer settlers would be about \$10,000. Including various pumps, tanks, taxes and delivery charges results in an estimated purchased equipment cost of \$96,000. Using standard factors for installation, instrumentation, control, piping, electrical, engineering and supervision, construction expense, contractors fees, startup costs, and contingency, a total capital investment (TCI) cost of \$383,000 was estimated. Varying the operating parameters has little impact on the TCI because of the system's relatively small size. The total annual operating costs (TAOC) for this full-scale A-LIX system were calculated as \$65,600 per year. The sensitivity of the TAOC to parameter variations are also low.

Using these costs, an annual savings of \$121,000 can be realized if WR-ALC does not have to dispose of 276 tons of sludge each year, which is attributed to presence of  $\text{Cr}^{\text{VI}}$ . These savings, together with the TCI and TAOC result in an estimated payback periods of 4, 7, and 10 years for the best, nominal, and conservative cases respectively. Increases in waste sludge disposal costs would result in the A-LIX system becoming even more attractive economically. For example, a 50 percent increase in the disposal costs would reduce the estimated payback periods to 2, 3, and 4 years. Capital cost savings may be possible by complete shop fabrication of the small system to minimize field construction, and piping costs..

### CONCLUSIONS AND RECOMMENDATIONS

The results of the A-LIX field-testing indicate that a 50-ppb  $\text{Cr}^{\text{VI}}$  effluent target can be consistently met under the following operating conditions: feed throughput of 600 ml/min or less, E/A ratio of at least 1/6, extraction pH of ~4.5, and strip pH of ~11, 5 percent Alamine® 336 concentration, and 2 Extraction units.

In addition, it was demonstrated that the system could produce a concentrated  $\text{Cr}^{\text{VI}}$  product of at least 20,000-ppm without disrupting the production of the <50 ppb effluent.

With the success of the A-LIX pilot plant operation, it is recommended that either OC-ALC, OO-ALC, or WR-ALC be chosen as the site for construction of a prototype A-LIX unit. (At Tinker or Hill, the A-LIX system would take the place of the current  $\text{Cr}^{\text{VI}}$  pretreatment systems.) The unit would be of commercial grade construction and design, and would require minimal operator attention. This prototype unit would be used to generate long-term continuous performance data, and generate  $\text{Cr}^{\text{VI}}$  concentrate for reuse/recycle evaluation. From this system,

detailed design and economic analysis could be developed, so that "turn key" units and operational procedures would be available to other sites.

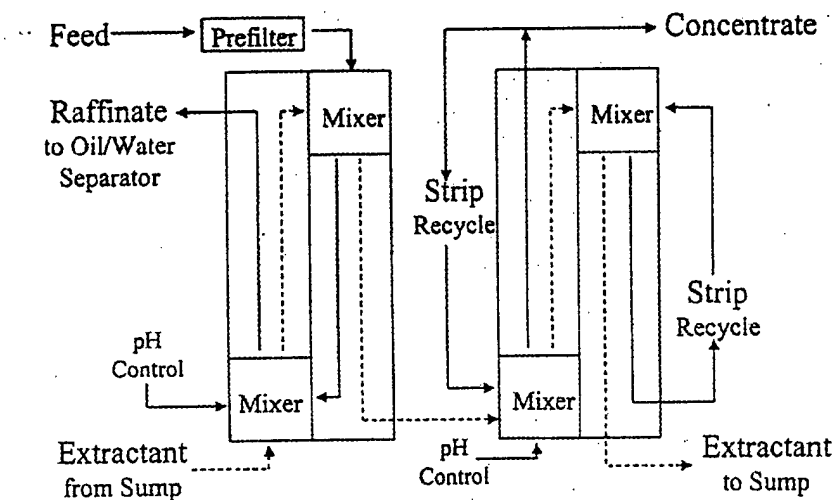


Figure 1. A-LIX Test System.

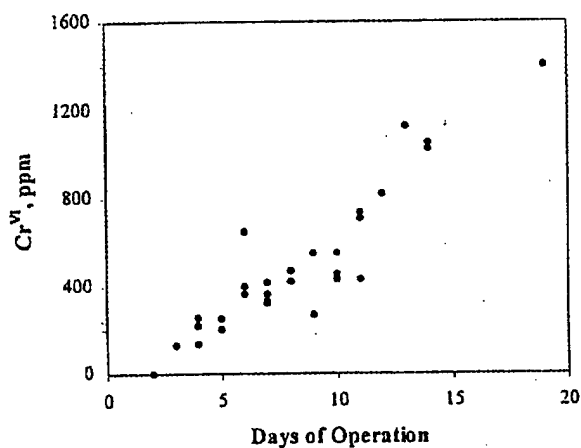


Figure 2.  
A-LIX Results:  $\text{Cr}^{\text{VI}}$  Accumulation in the First Stripping Stage.

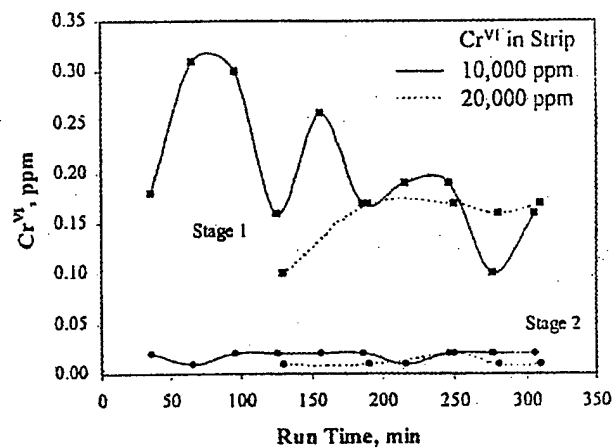


Figure 3.  
A-LIX Removal of  $\text{Cr}^{\text{VI}}$  from a Feed Concentration of 6.4 ppm.

**TABLE 1. RESULTS OF A-LIX FIELD-TESTING.**

Sample Number	Feed Cr <sup>VI</sup> ppb	Feed Flow Rate ML/min	pH	E/A Ratio	Raffinate [Cr <sup>VI</sup> ], ppb Average
1	3900	505	3.5	1/5	37
2	2900	516	3.5	1/5	<10
3	6400	516	3.5	1/5	14
4	6400	516	3.5	1/7	25
5	10,500	775	3.5	1/6	178
6	7000	646	3.2	1/6	40
7	4600	644	3.3	1/6	27
8	4600	505	3.2	1/9	32
9	6400	514	3.5	2/9	18
10	6400	500	3.3	1/4	12
<b>Average</b>	<b>5900</b>	<b>564</b>	<b>3.4</b>	<b>1/6</b>	<b>38</b>

**TABLE 2. ACCUMULATED SPECIES IN THE STRIP SOLUTION.**

Actual Product Solution is expected to be at least 20,000 ppm in Cr<sup>VI</sup> (see text).

Constituent	Concentration, ppm
Total Organic Carbon	613
Fluoride	1.95
Sulfate	15,500
Total Kjeldahl Nitrogen	20
Aluminum	8.09
Calcium	11.6
Cadmium	< 0.01
<b>Chromium (VI)</b>	<b>1,400</b>
Copper	0.17
Iron	0.84
Magnesium	1.30
Manganese	0.12
Nickel	0.97
Lead	0.69
Zinc	0.25